COMPOSITIONAL DEPENDENCE OF THE THERMAL STABILITY AND RELATED PROPERTIES, OF METALLIC GLASSES I: T_g FOR $Ca_{.65}M_{.35}$ AND $Zr_{.475}Cu_{.475}M_{.05}$ GLASSES,

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COMPOSITIONAL DEPENDENCE OF THE THERMAL STABILITY AND RELATED PROPERTIES

OF METALLIC GLASSES I: T_g FOR $Ca_{.65}M_{.35}$ AND $Zr_{.475}Cu_{.475}M_{.05}$ GLASSES

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INTRODUCTION

The stability of metallic glasses at ambient and elevated temperatures is a property of considerable practical as well as theoretical importance. Consequently, the thermal effects occurring on heating of metallic glasses are among their most commonly determined characteristics.[1,2] As for the phase transformations (especially melting) of most crystalline metals and alloys, however, the understanding of these effects, especially their correlation with other properties, is not yet well developed, although progress has been made in individual cases.[1,3-5]

One may distinguish two types of thermal effects: exothermic (crystallization, recrystallization, relaxation) and endothermic (glass transition). Of these, the former are complex in that they pertain to reactions involving more than one phase at the same time; accordingly, they generally differ from glass to glass and can not be easily treated quantitatively. The latter, however, is a reversible effect which occurs within a homogeneous phase and should therefore be amenable to a general treatment. Such a treatment would then establish correlations of three types: (a) between the glass transition temperature T_g and related properties of the glass itself such as elastic moduli;[3-5] (b) between T_g and physical-chemical properties of the alloy system, such as phase diagram features[6] (e.g. the presence of intermediate phases and their melting points) and thermodynamic quantities of the system;[7] (c) between T_g and appropriate parameters of the constituent elements.[4,5] Relations of types (b) and (c) can be expected to have predictive character concerning T_g without the glass actually having been formed; relations of type (c) would be the most generally useful. (It should be pointed out that in the absence of T_g values, correlations of types (a) - (c) have been attempted for the crystallization temperatures T_c.[8-10])

To examine the validity of such correlations, one fruitful approach is to compare the T_g's of binary glasses in which one component and the stoichiometric ratio are held fixed while the other component is varied. Studies of T_g, however, are confronted with the difficulty that only a rather small number of binary glassy alloys display glass transitions, especially well pronounced ones [i.e. glass transitions with a sufficiently large interval $(T_c - T_g)$[11]]; these alloys include Pd-Si,[12] Zr-Cu,[3,4,13] and, Ca-Al and Ca-Zn glasses[6,14] which were discovered only recently. On the other hand, while glasses containing three or more components at substantial concentrations more frequently show glass transitions,[7] such alloys are also more likely to have more complex interactions of the components; at the present state of this field, they are therefore less suitable than binary glasses to examine such correlations.

81 4 30 203

There are two approaches, both involving ternary systems, by which additional T_g data usable for comparative studies can be obtained: (1) deduction of the T_g values for binary glasses from studies of suitable ternary systems[1,7] and (2) ternary additions (at levels from 0-20 at.pct.) to binary glasses displaying a glass transition.[15] In the work reported in the present paper, the first approach has been applied to $Ca_{.65}M_{.35}$ glasses; $Zr_{.475}Cu_{.475}M_{.05}$ glasses were studied as an example of the second approach.

$Ca_{.65}M_{.35}$ Glasses (M = Pd; Cu, Ag, Au; Mg, Zn; Al, Ga)

It had recently been reported that Ca readily forms binary glasses with a number of metallic elements M added at levels, depending on the system, of ~ 15 to ~ 60 a/o M;[6,14] the list of metals M includes A metals (Mg), transition metals (Ni, Pd), and B metals (Cu, Ag, Au, Zn, Al, and Ga).[6,14,16] The formation and alloy chemistry of many of these glasses have been discussed and a survey of their crystallization behavior has been given;[6] the crystallization sequences of some glassy Ca alloys were found to be quite complex, displaying up to five exothermic steps for some compositions.[14,16]

In this survey, well defined glass transitions were found in two binary Ca alloy systems, Ca-Zn and Ca-Al.[6,14] The glass transitions in the Ca-Al and Ca-Zn systems are observable for $0.30 \leq x_{Al} \leq 0.45$, and $0.20 \leq x_{Zn} \leq 0.60$, respectively; in all other Ca systems (with the possible exception of Ca-Au at relatively high Au concentrations[16]) T_g is masked by crystallization or other exothermic processes. At high Ca concentrations, the crystallization temperatures drop rapidly, masking T_g even in the Ca-Al system at $x_{Al} < 0.30$.[14]

The composition $Ca_{.65}M_{.35}$ was selected for a comparative study. To obtain the T_g values of interest despite the overlapping exothermic effects in the respective binary Ca systems, ternary alloys of the composition $Ca_{.65}(Al_{1-y}M_y)_{.35}$ were studied in the hope, first, of being able to retain ternary glasses at the desired composition $x_{(Al+M)} = 0.35$ over a wide range of y values and, second, to be able to determine T_g for binary $Ca_{.65}M_{.35}$ by extrapolation from the ternary $Ca_{.65}(Al_{1-y}M_y)_{.35}$ alloys. For M = Cu, alloys of composition $Ca_{.65}(Zn_{1-y}M_y)_{.35}$ were also studied.

$(Zr_{.50}Cu_{.50})_{0.95}M_{.05}$ Glasses (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu)

The second approach to providing interpretable T_g data, wherein the change in T_g upon the addition of alloying elements to glasses displaying glass transitions is determined, was used in a study of T_g for Pd-Si-M glasses;[12,15] it was also employed to examine the effect of alloying additions on T_c in Fe-C-P-M glasses (M = transition metals)[8] and in Mg-Zn-M glasses (M = B metals).[17] A corresponding study for Zr-Cu-M glasses has now been carried out[4] wherein the well pronounced glass transition of binary $Zr_{.50}Cu_{.50}$ glass[3,13] was utilized. The effect of ternary additions of first period transition metals M at a level of 5 at.pct. to form $Zr_{.475}Cu_{.475}M_{.05}$ glasses is reported here.

EXPERIMENTAL METHODS

All alloys were initially prepared by arc-melting using 99.9% pure starting materials (with the exception of Zr which was 99.7% purity reactor grade material). Weight loss analyses indicated agreement between the nominal and actual composition to ≤ 1 at.pct.

For Ca alloys, glasses were prepared by melt spinning[18] in a vacuum of ~ 50 µm Hg; ribbons of ~ 2 mm width and ~ 50 µ thickness were formed during solidification on the inside of a copper drum. For Zr-Cu alloys, amorphous foils were

prepared by arc furnace hammer-and-anvil quenching.[19] All ribbons or foils
selected for thermal analysis exhibited no evidence of crystalline portions
when examined by XRD (to the detection limit of this method, estimated at
several %). Differential scanning calorimetry (DSC) was carried out on a Perkin-
Elmer DSC2 at $\dot{T} = 80$ K/min; the glass transitions reported here were determined
by the midpoint method (point of inflection of the endotherm). Crystallization
temperatures T_c were determined as onset temperatures (steepest tangent method).

RESULTS

T_g for $Ca_{.65}(Al_{1-x}M_x)_{.35}$ Glasses

The desired ternary glassy Ca alloys were prepared in eight systems which
are reported here. $Ca_{.65}(Al_{1-y}M_y)_{.35}$ glasses, with M = Pd, Cu, Ag, Au, Mg,
Zn, Ga, and $Ca_{.65}(Zn_{1-y}Cu_y)_{.35}$ glasses were prepared. Glasses in seven of
these eight systems showed glass transitions up to y ∿ 0.75; the exception was
the $Ca_{.65}(Al_{1-y}Cu_y)_{.35}$ system, where T_g was observable only for y ≤ 0.25. In-
stead of the latter system, $Ca_{.65}(Zn_{1-y}Cu_y)_{.35}$ glasses were therefore studied
yielding T_g values up to y = 0.67. An example of the DSC results obtained on
such ternary alloys is given in Figure 1 for the $Ca_{.65}(Al_{1-y}Au_y)_{.35}$ system.
The multiple exothermic effects and the decrease of the initial T_c to values
below T_g at y ∿ 0.85 (thus masking T_g) can be seen. It is also apparent that
the observed T_g have a parabolic dependence on y. T_g was therefore fitted to
the expression:

$$T_g(y) = (1-y)T_g(Ca_{.65}Al_{.35}) + y \cdot T_g(Ca_{.65}M_{.35}) + \lambda \cdot y(1-y).$$

Expressions of this type have been used before for ternary glasses.[1,7] The
fit with the experimental points was excellent (see Figure 1) and the values
for $T_g(Ca_{.65}M_{.35})$ obtained by extrapolation are thought to be precise within
the assumed functional relationship to ± 10 K. The resulting $T_g(Ca_{.65}M_{.35})$
are shown in Figure 2, where they are plotted together with the values obtained
directly for the two binary glasses $Ca_{.65}Al_{.35}$ and $Ca_{.65}Zn_{.35}$ against the
valence of the addition element M (see below).

A presentation and further discussion of the ternary data, especially of
the interaction coefficients λ, will be given elsewhere.

T_g for $(Zr_{.50}Cu_{.50})_{.95}M_{.05}$ and T_c for $(Zr_{.50}Cu_{.50})_{.975}M_{.025}$ Glasses

$(Zr_{.50}Cu_{.50})_{1-x}M_x$ alloys (where M represents transition metals of the
first long period from Sc to Ni) with M contents corresponding to 2.5, 5, and
10 a/o were studied.[4] Glasses were obtained at all levels for all of these
additives, with the exception of the alloy containing Sc at x = .10 which was
partly crystalline; further, glass transition temperatures could not be re-
liably determined for glasses containing V and Cr at this level.[4] At x = .05,
however, glass transition temperatures could be obtained for all additives;
these values as well as the crystallization temperatures of $(Zr_{.50}Cu_{.50})_{1-x}M_x$
glasses with x = .025 are reported and discussed here. Results on additional
ternary alloys of this type, also including non-transition metal additives, will
be reported subsequently.

Values for $\Delta T_g = T_g(Zr_{.475}Cu_{.475}M_{.05}) - T_g(Zr_{.50}Cu_{.50})$ were calculated,
using a value of $T_g(Zr_{.50}Cu_{.50}) = 692$ K. The resulting ΔT_g are plotted against
the periodic table position (group number) of M in Fig. 3a. From the measured
temperatures of the onset of crystallization, values for
$\Delta T_c = T_c(Zr_{.4875}Cu_{.4875}M_{.025}) - T_c(Zr_{.50}Cu_{.50})$ were calculated, using
$T_c(Zr_{.50}Cu_{.50}) = 737$ K; these ΔT_c values are presented in Fig. 3b. The over-
all similarity of the curves for ΔT_g (presented here for x = .05) and ΔT_c (at

x = .025) as functions of M is apparent, indicating a similar effect of M in both transitions. (The similarity between ΔT_g and ΔT_c was somewhat le s pronounced when both curves were taken at x = .05.) Further, for most of the addition elements M studied here, the curves of ΔT_g and ΔT_c vs x are not linear. This made it necessary to give ΔT_g and ΔT_c at a specific value of x rather than presenting the slope dT_g/dx, as is customary for linear changes of T_g with x;[1],[7] the values of ΔT_g and ΔT_c given here are not quantitatively representative of the effect of M on T_g and T_c at other addition element concentrations.

DISCUSSION

Correlations of T_g with Other Alloy Parameters

It had been noted previously[3] that the thermal stability, and especially, T_g, of the metallic glasses which were studied correlates with their elastic properties; thus, T_g and the Young's modulus E both increase with increasing Cu content in amorphous Zr-Cu.[3],[20] Further, the thermal stability of the glass has been related to the melting behavior of the corresponding crystalline alloy; thus, T_g (and T_c) often increases with increasing melting point T_m of the alloy, as suggested early by Mader[21] (for a review, see Ref. 22) and as confirmed recently for glasses containing actinides,[10] refractory metals,[9] and, now, Ca.[6]

These connections between T_g, T_m, and E suggest that the glass transition resembles the melting process in being related to the elastic properties of the solid. For crystalline alloys, such a connection is described by the Lindemann melting point formula,[23] which relates T_m to the Debye temperature Θ_D and/or E.[24-26] It has recently been considered that an analogous relation might hold for T_g, linking T_g to E, and, hence, to T_m.[5] This idea has considerable appeal: in some respects, a Lindemann-type equation may be more applicable to the glass transition than to the melting process; the atomic processes[27] thought to take place during the rearrangement of free volume at T_g appear to be more amenable to an analysis based on elastic forces, which underlies the Lindemann T_m formula, than the melting process. Furthermore, a fundamental criticism of the Lindemann T_m formula is that it is a "single phase" formula, i.e. an expression using only parameters of the solid, although it is applied to a two-phase process. The glass transition, on the other hand, occurs within a single phase; it does not involve the total rearrangement of the structure which occurs during the melting process, and it therefore comes much closer to the physical picture on which the Lindemann T_m formula is based.

In the following section we briefly review the Lindemann T_m formula and present modifications required for its application to T_g, with specific reference to metallic glasses having compositions typical of the two families of glasses treated here.

The Lindemann T_m Formula and its Modification for Application to T_g

The Lindemann formula for the melting point T_m of an element M is:[23-26]

$$T_m = L \cdot m_M \cdot \Theta_D^2 \cdot V_M^{2/3} \tag{1}$$

where L is a constant (Lindemann constant), m_M is the atomic mass of M, Θ_D is the Debye temperature, and V_M is the atomic volume of M. From this expression, a relation to the elastic parameters can be derived[25] which yields:

$$T_m = L' \cdot E \cdot V, \tag{2}$$

where E is the Young's modulus of M. For the first case of interest here, a

binary glass $A_{1-x}B_x$, an expression of the form

$$T_g = h(r_A/r_B) \cdot E \cdot V_B \qquad (3a)$$

can be derived, where E is the Young's modulus of the glass, V_B is the atomic volume of the smaller component, and $h(r_A/r_B)$ is a relatively slowly varying function of the atomic size ratio r_A/r_B. For the special case of relatively weakly interacting atomic species, the elastic constants may be assumed to be approximately additive; hence

$$E = \alpha \cdot \bar{E}$$

and

$$T_g = h(r_A/r_B) \cdot \alpha \cdot \bar{E} \cdot V_B \qquad (3b)$$

where $\bar{E}$ is the weighted averaged E of the components in their crystalline form and α is a constant factor ($\alpha \sim 0.7$)[28] relating E for a glass to that of the corresponding crystal or crystal mixture.

Using the solidus melting temperature T_S (frequently a eutectic temperature) for the glass forming composition and making the doubtful assumption that the melting mechanism is similar to that for the glass transition, one obtains

$$T_g = k_1 \cdot T_S, \qquad (3c)$$

as frequently (but no universally) found[22] (see below).

Turning to the second case of interest here, ternary additions M at level x_M to a binary glass $A_{1-y}B_y$, and again assuming weak interactions between M and A or B, one obtains

$$\frac{\partial \ln T_g}{\partial x_M} = F_{AB}(E_M, V_M, m_M) \qquad (4a)$$

where E_M, V_M and m_M are the Young's modulus, atomic volume, and atomic mass of the addition element M, respectively, and F_{AB} is a function dependent on the properties of the binary glass $A_{1-y}B_y$.

An especially simple relationship of this type for which there is some theoretical justification expresses $\Delta T_g(x_M)$ by

$$\Delta T_g(x_M) = A_M \cdot E_M \cdot V_M^{1/3}; \qquad (4b)$$

where A_M is a function of M that contains m_M. Substituting $T_m(M)$, the melting point of M, for its elastic modulus, using (2), one obtains from (4b)

$$\Delta T_g(x_M) = (A_M/L') \cdot T_m(M)V_M^{-2/3}. \qquad (4c)$$

T_g for $Ca_{.65}M_{.35}$ Glasses

We discuss the T_g values for these glasses presented in Fig. 2, and we review correlations of T_g with pertinent alloy parameters, beginning with those discussed in the preceding section and continuing with alternate variables such as compound melting points or alloy valence.

Elastic Modulus E: At present, E values for the $Ca_{.65}M_{.35}$ glasses as required in Eq. (3a) are not yet available; however, they are being determined.[20] Expressions such as (3b) which contain only the elastic constants of the components instead of E for the glass are not applicable to the present systems

because the components show significant interactions which vary from system to system; accordingly, T_g and $\bar{E}$ do not correlate.

Solidus Temperature T_S: A possible correlation of T_g with T_S, the solidus temperatures of the binary systems Ca-M at 35 at.pct. M, according to Eq. (3c), is tested in Figure 4. [For Ca-Au, T_S increases from 931 K for $x_{Au} < 0.333$ (Ca_2Au) to 1073 K for $x_{Au} > 0.333$; an averaged value $T_S \sim 1000$ K was therefore used to remove this discontinuity.] It is seen that T_g for M = Zn, Mg, Cu, Ag, and Au lies on or close to a straight line with $T_g/T_S = 0.58$; this value for T_g/T_S is in good agreement with other values observed for T_g/T_S.[22] The T_g values for the trivalent M elements Al and Ga (especially Al) do not follow this relation: for these elements T_g is either higher or T_S is lower than given by the correlation (or both). This suggests that both the melt and the glass are strongly stabilized with respect to the crystalline phase or phases in the Ca-Al and Ca-Ga systems. To explain the observed T_g values, further study of pertir thermodynamic quantities would be useful, including an assessment of phase diagram features affecting T_S in these systems.

Melting Temperatures T_m of the Compound CaM_2: From the relations suggested by Eq. (3b) and (3c) we turn to a correlation of T_g with a phase diagram feature other than T_S. Inspection of the phase diagrams of the present Ca-M systems which form glasses in their Ca rich regions shows that in all of these systems, except Ca-Cu, the M rich regions contain CaM_2 phases. Four of these phases, in the systems with M = Mg, Zn, Al, and Ga, are Laves phases with relatively high melting points. To test for a possible correlation between the thermal stabilities of the glass and the CaM_2 phases, T_g was plotted against the melting points $T_m(CaM_2)$ (Figure 5). For the systems with Ag and Au, averages of the T_m for two phases adjacent to and more stable than CaM_2 were used; for Ca-Cu the liquidus at the composition $CaCu_2$ was used as an upper bound for T_m. With these provisos, a fair correlation of T_g and $T_m(CaM_2)$ was found, with $T_g/T_m(CaM_2) \sim .42$; existence of this correlation may reflect the consideration expressed earlier[6] that formation and stability of glasses in the Ca systems (and other similar systems) is related to the presence and stability of a Laves phase by complementary aspects of packing and bonding.

Relation of T_g with Other Parameters: The size ratio of the components in Ca-M glasses has been shown[6] to correlate well with the width of the glass forming range and might also be expected to affect glass stability, as reported, e.g., for Laves phases;[29] however, no correlation between T_g and $r_{12}(Ca)/r_{12}(M)$ is apparent.

T_g was also plotted against $\overline{\Delta H_c}$, the averaged cohesive energy of the glass components; a straight line relation including the origin was found, with a scatter comparable to that seen in Fig. 4. The principal departures from this straight line were observed for Cu and Ag, for which T_g was ~ 100 K lower than predicted from their cohesive energies.

Alloy Valence: It is likely that better correlations than those presented here are not possible until measurements on the elastic properties of the Ca-M glasses are available or more thermodynamic information on the Ca-M alloy systems is available. In the meantime, it is instructive to consider the thermal stability of the Ca-M glasses in terms of the valence n of element M, or in terms of the average valence electron concentration (VEC) (Figure 2). The VEC also plays an important role in the Nagel-Tauc theory relating glass formation and stability to VEC ~ 2 e/a.[30]

The plot shows the following features, discussed in order of decreasing valence of M:
a) Glasses of Ca with Si and Ge, n=4, would be expected to be very stable.

However, for chemical reasons, such glasses could not yet be prepared.

b) Al and Ga, n = 3, form stable glasses with Ca.

c) Mg and Zn, n = 2, form the least stable glasses with Ca prepared in this study.

d) For Cu, Ag and Au, n = 1, T_g increases again; this increase, however, is due to the bond strength inherent in these metals [due (for Cu) in roughly equal parts to conduction electron bonding and s-d hybridiza-tion[31]); this bond strength appears to be retained in the glass. A glass of Ca with a simple monovalent (alkali group) metal has not yet been prepared; it is assumed that its thermal stability would be lower than that of the Ca-Mg glass, as indicated for Na.

e) Pd, assigned n = 0, as frequently done in the classification of compounds formed by Ni group metals with simple metals such as Zn,[32] forms the most stable glass; this results mainly from the d – electron bonding contribution of Pd to the glass.

f) Besides its valence, the size of M plays a major role; for each group of M metals, T_g increases with increasing size of M (Zn → Mg; Cu → Au). T_g for Ca-Ag is especially interesting; although the size of Ag should place T_g near T_g(Ca-Au), the lower bond strength of Ag (expressed e.g. in its cohesive energy[33]), as compared to Au, moves T_g(Ca-Ag) down to T_g(Ca-Cu).

T_g for $Zr_{.475}Cu_{.475}M_{.05}$ Glasses

The ΔT_g data in Fig. 3a are discussed in terms of the elastic moduli E_M and atomic volumes V_M of the addition elements M (data from Ref. 35) and equa-tions (4b) and (4c) are applied. Values for Zr and Cu considered as "ternary additions" are also included; these were derived from data on the binary Zr-Cu system.[4,13]

A similar study of the effect of transition metal additives from the second long period is now in progress.

Elastic Moduli and Atomic Sizes of M: The qualitative similarity of the plots for ΔT_g, ΔT_c, and E in Figure 3 (a-c) suggests that these quantities are indeed interrelated; the characteristic, bimodal appearance of all three plots is familiar from the plots of other properties of the first long period tran-sition elements[33] (cohesive energy, bulk modulus) and its recurrence here is striking. In comparing the plots for ΔT_g and E in Fig. 1, disagreements in de-tail are seen, particularly for V and Cu; for both of these ΔT_g is considerably larger than suggested by E.

The quantitative connection established by the relation (4b) is tested in Figure 6, which shows a plot of ΔT_g vs. $E_M \cdot V_M^{1/3}$. There is a fairly good linear relationship between these two quantities, except for V and Cu which depart strongly from this relationship as noted already for E_M; both elements are more effective in stabilizing the Zr-Cu glass than is indicated by their elastic moduli and atomic sizes. The larger effect of Cu may be due to its B-metal character (see below); for V the melting temperature represents the stabilizing effect better than the low Young's modulus E (see below) or any of the other elastic moduli G or B.[33]

Melting Temperatures $T_m(M)$: The previous section suggests that the present Zr-Cu-M glasses (M = transition metal) are largely additive in their elastic properties which affect T_g. It is therefore of interest whether the elastic constants of the addition elements can be replaced by the corresponding melting temperatures $T_m(M)$ following Eq. (2).

The relation of ΔT_g to $T_m(M)$ given by Eq. (4c) is tested in Fig. 7, where ΔT_g is plotted against $T_m(M) \cdot V_M^{-2/3}$. For all transition metal additives, the ΔT_g values are seen to follow a common curve with relatively little scatter; only Cu departs from this curve, showing again a greater stabilizing effect than would be suggested by its melting point (see below). In contrast to the relation of ΔT_g with E_M, previously discussed, the value for V now follows the common curve, indicating that its glass stabilizing effect is more closely related to its melting point than its elastic modulus. The good overall fit of the ΔT_g data with Eq. (4c) strongly suggests that the glass stabilizing effect and the melting points of the transition metal additives in the present glasses are indeed interrelated.

Other Relations: We note that a fit of ΔT_g to the cohesive energies, even if evaluated in connection with an empirical volume factor, provides less over-all agreement than the correlations with E_M and $T_m(M)$ discussed in the two previous sections; thus the observed stabilizing effect of Cr and the strong destabilizing effects of Sc and Ti are underestimated, and the (smaller) stabilizing effects of the late transition elements are overstimated.

Non-Transition Metal Additives: A comprehensive study of the effect of B-metal and metalloid additives on T_g for $Zr_{.50}Cu_{.50}$ is in progress.[34] Initial results[4] show that several non-transition metal addition elements have strong stabilizing effects; the magnitude of these effects, however, is not well correlated to their elastic properties and melting points but depends on other pertinent properties such as valence, again in combination with size. The effect of these addition elements thus resembles in some respects that of the B-metal and coinage metal components in the Ca-M glasses treated above; as for the latter, correlations of T_g with phase diagram features (compound formation and stability) may also exist for the Zr-Cu-M glasses. An example is Al which causes a thermal stabilization of the Zr-Cu glass larger than that produced by any of the T-metal addition elements at equal levels; the corresponding T_g value falls far above that given by either of the curves in Figure 6 and 7. The strengthening effect of Cu as an additive in Zr-Cu-M alloys noted above probably has the same origin as that of the other B-metals.

We will not comment here on possible alloy chemical reasons for the difference between the effects due to the two groups of additives. In any case, it appears that for the non-transition metal additives the interactions between the additive and the transition metal combination forming the "basic" glass are no longer negligible as they seem to be for transition metal additives, and hence Eq. (3b), (3c), (4b), and (4c) do not apply.

CONCLUSION

Ternary alloy glasses have been studied to obtain T_g values for binary Ca glasses not displaying a glass transition. The results show that for $Ca_{.65}M_{.35}$ glasses T_g depends on alloy valence and size; some correlations to phase diagram features such as the solidus temperature and the melting points of the phase CaM_2 were also observed.

It was also shown that for first long period transition metal additives to a $Zr_{.50}Cu_{.50}$ glass the changes of T_g and T_c are closely related to each other and, jointly, to the elastic moduli and melting points of the additives; the changes of T_g are in general agreement with the predictions of an expression for T_g which is based on a modification of the Lindemann melting point formula appropriate for the glass transition.

The present results suggest that the properties controlling the thermal stability of glasses are additive when transition metal elements are added to

a binary glass such as Zr-Cu, while interaction terms must be considered for non-transition metal addition elements as well as for most Ca-M glasses.

The study of the thermal stability (and elastic properties) of metallic glasses may provide a general approach enabling one to determine the bonding effect of alloying additions at low and high levels without the restrictions on single phase formation imposed by the phase diagram.

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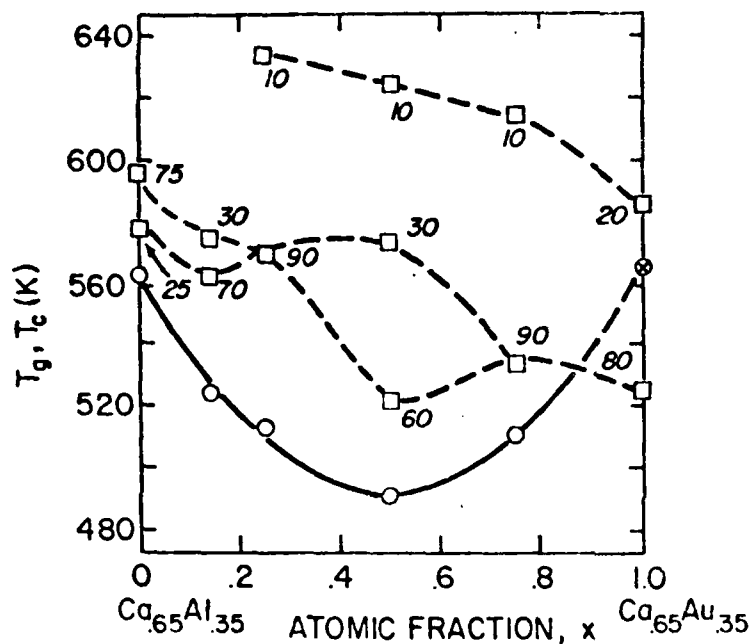
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Fig. 1. Glass transitions T_g(o) and exothermic effects (□) in ternary $Ca_{.65}(Al_{1-x}Au_x)_{.35}$ glasses. The T_g values are fitted with the parabolic curve shown as solid line (see text) so as to determine T_g for $Ca_{.65}Au_{.35}$. The dashed connections of the exothermic effects are tentative; some connected exothermic effects may not correspond to related physical processes.
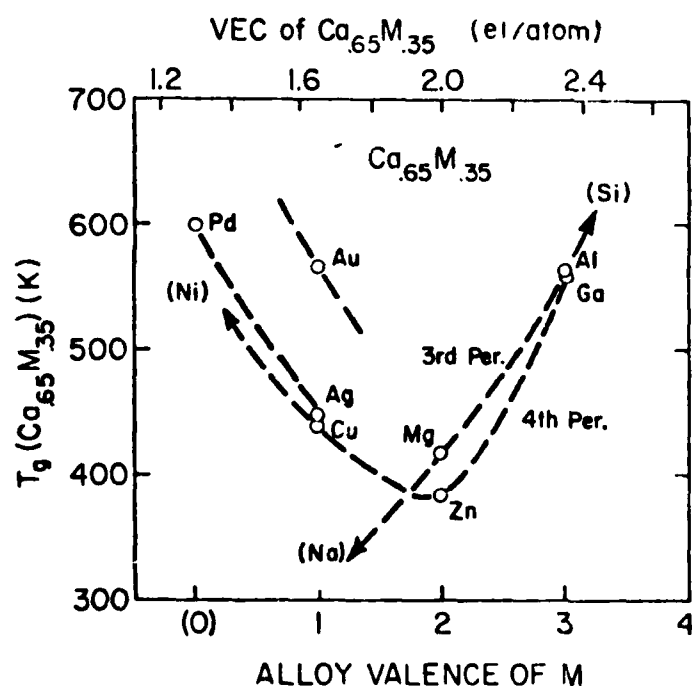
Fig. 2. Glass transition temperatures T_g for binary $Ca_{.65}M_{.35}$ glasses derived from binary or appropriate ternary systems (see text), plotted against the valence of M (bottom) and the average valence electron concentration (VEC) of the glass (top). Here, Pd is assumed to have a valence of zero.[32]
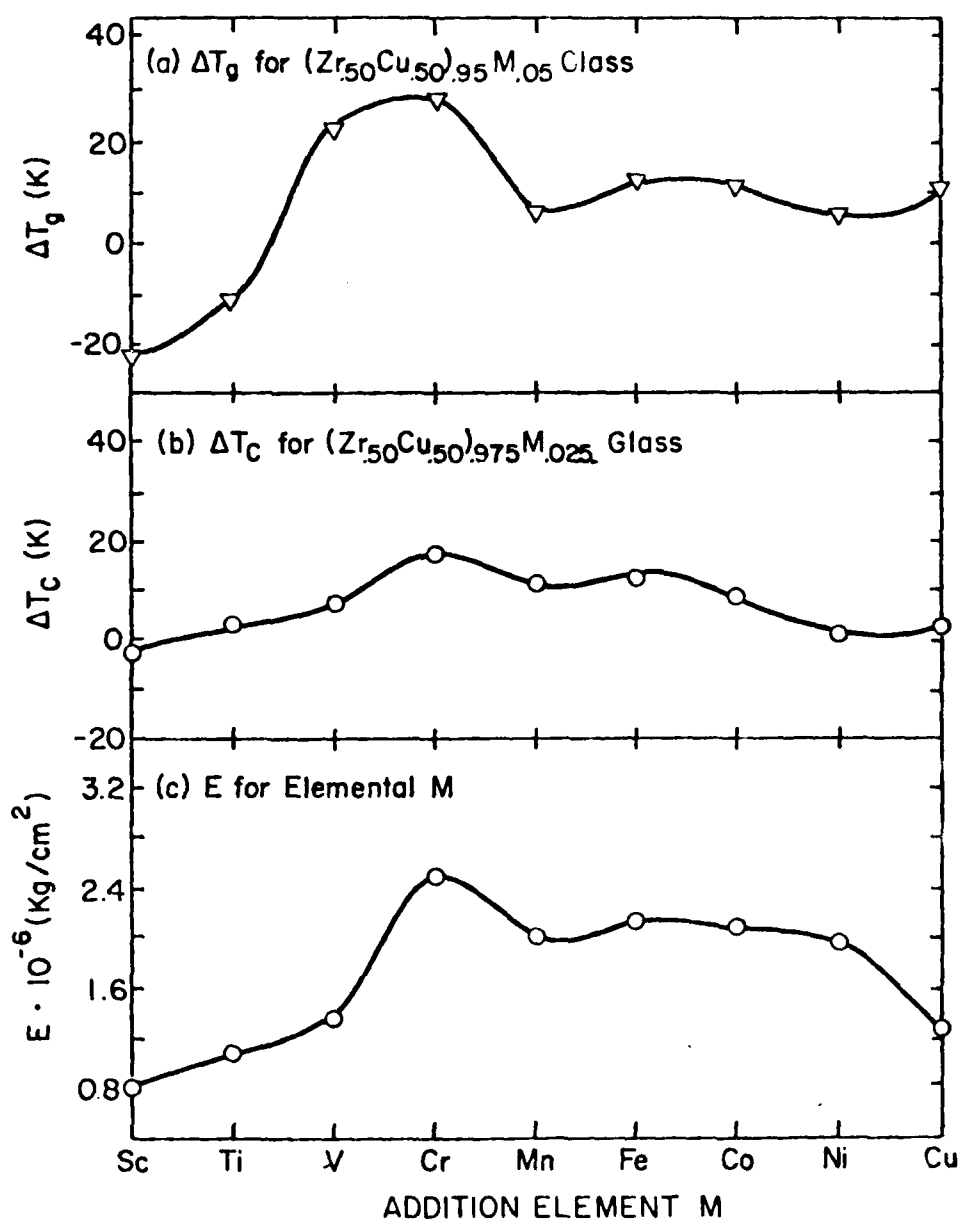
Fig. 3. Properties of Zr-Cu-M glasses (a,b) and crystalline
M (c) plotted against M, transition elements from the first
long period.
(a) $\Delta T_g(Zr_{.475}Cu_{.475}M_{.05}) = T_g(Zr_{.475}Cu_{.475}M_{.05}) - T_g(Zr_{.50}Cu_{.50})$
(b) $\Delta T_C(Zr_{.4875}Cu_{.4875}M_{.025}) = T_C(Zr_{.4875}Cu_{.4875}M_{.025}) - T_C(Zr_{.50}Cu_{.50})$
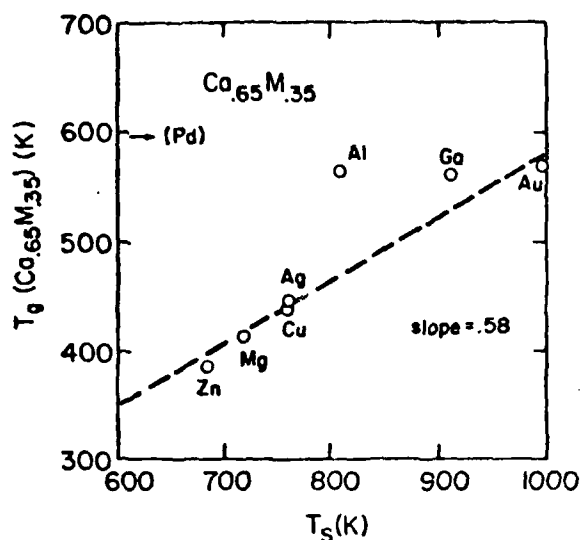(c) Young's modulus E for crystalline, elemental M.

Fig. 4. Glass transition temperature T_g of $Ca_{.65}M_{.35}$ glasses plotted against the solidus temperatures T_S.[6]
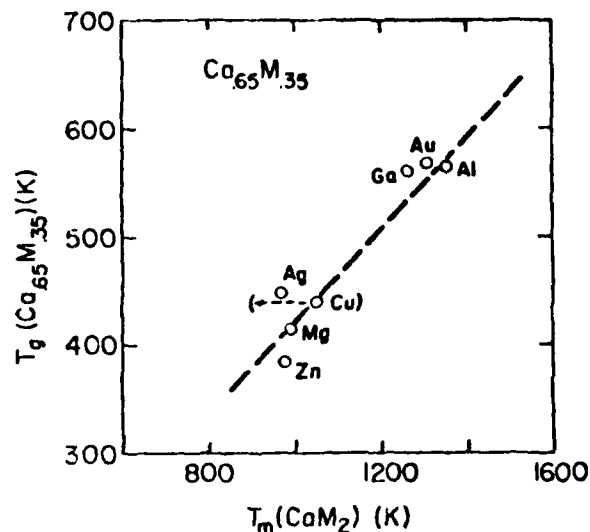

Fig. 5. Glass transition temperature T_g of $Ca_{.65}M_{.35}$ glasses plotted against T_m, the melting temperatures of CaM_2 (see text for explanation for M = Cu Ag, and Au).
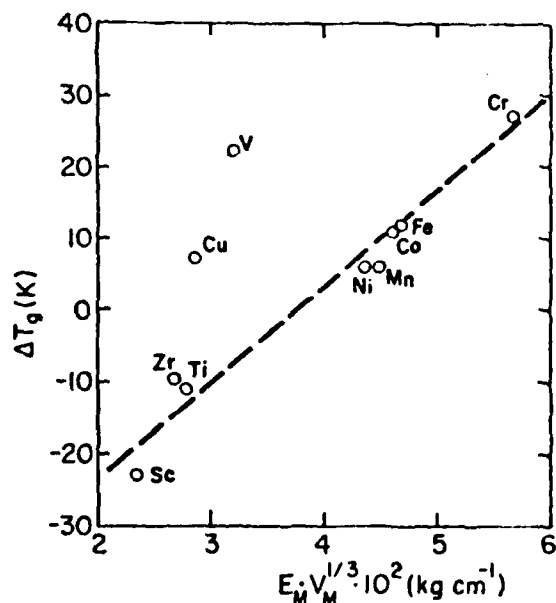

Fig. 6. ΔT_g for $(Zr_{.50}Cu_{.50})_{.95}M_{.05}$ glasses (as defined in Fig. 3) plotted against $E_M \cdot V_M^{1/3}$, where E_M = Young's modulus of M, V_M = atomic volume of M.
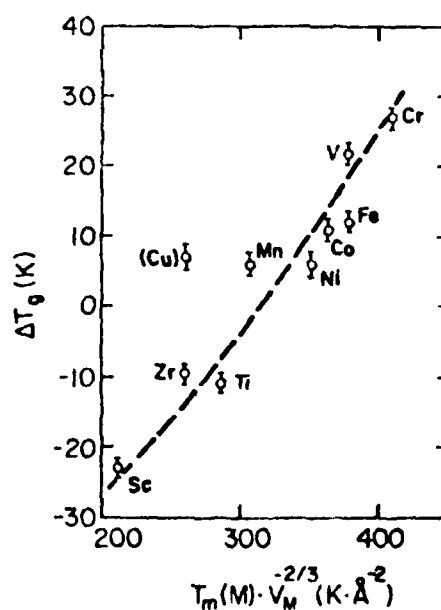

Fig. 7. ΔT_g for $(Zr_{.50}Cu_{.50})_{.95}M_{.05}$ glasses (as defined in Figure 3) plotted against $T_m(M)V_M^{-2/3}$ where $T_m(M)$ = melting temperature of M, V_M = atomic volume of M.

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8